

IRON-BASED CATALYSTS FOR SLURRY-PHASE FISCHER-TROPSCH SYNTHESIS

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Introduction

The Pittsburgh Energy Technology Center is responsible for implementing the U.S. Department of Energy's (DOE) Indirect Liquefaction program as part of the Coal Liquefaction program. The overall goal of the Coal Liquefaction program is to develop the scientific and engineering knowledge base to help industry market economically competitive and environmentally acceptable advanced technology for the manufacture of synthetic liquid fuels from coal.

This article examines the state of knowledge in iron-based catalysts for use in slurry-phase synthesis reactors used in the Indirect Liquefaction of coal. The advantages of using iron catalysts are (1) they are inexpensive, (2) specific activity for Fischer-Tropsch (FT) synthesis is high, and (3) some iron catalysts have high water-gas-shift activity and can convert low H_2/CO ratio synthesis gas without an external shift reaction step.

Stoichiometry of the FT Reaction:

The intrinsic stoichiometry of the FT synthesis reaction is represented by eq 1. Many FT catalysts are also active for water-gas-shift (WGS) reaction represented by eq 2. Catalysts that are active for both reactions can be used to convert synthesis gas with hydrogen-to-carbon monoxide ratios as low as 0.5 into hydrocarbon products [see eq 3]. This point is significant because of the development of several advanced coal gasification processes that directly produce synthesis gas with approximately this ratio.



In current commercial practice (SASOL, South Africa), the indirect liquefaction route for the conversion of coal to liquid fuels involves four principal stages [1], namely, coal gasification, gas purification, hydrocarbon synthesis, and product upgrading.

Of these, the gasification step is the most expensive; hence, technological improvements associated with this step offer the greatest potential for reducing costs.

A number of advanced gasification processes (e.g., Texaco and Shell-Koppers), which are now in various stages of commercial development, significantly improve on SASOL technology [2] which uses the conventional Lurgi gasifier. The advanced gasifiers not only exhibit improved efficiencies but also produce a smaller proportion of undesirable by-products (e.g., CH_4 , CO_2 , and H_2S). At the same time, however, the hydrogen-to-carbon monoxide ratio of the synthesis gas produced is much lower (0.5-0.9, compared to 2.1 for Lurgi). It has been shown that hydrocarbon products can be produced at reasonable reaction rates from this low H_2/CO synthesis gas [3-5], provided the catalyst is active for both reactions 1 and 2.

Depending on the process configuration, the desired products from slurry-phase FT synthesis could be liquid fuels (e.g., gasoline, diesel, jet fuel), light olefins, and/or wax. The light olefins could be oligomerized to liquid fuels through known processes such as MOGD [6]. The wax could be treated by catalytic hydrocracking to provide liquid fuels [7].

Slurry Phase FT Synthesis: The development of a slurry-phase Fischer-Tropsch process using an iron-based catalyst has drawn considerable attention. The advantages of the slurry-phase reactor system are (1) the ability to use low H_2/CO ratio synthesis gas produced by the advanced gasification processes, (2) the ability of the liquid phase to withdraw heats of reaction efficiently and thereby control reaction temperature, (3) high catalyst and reactor productivity, (4) favorable conditions for catalyst regeneration, and (5) simple construction and low investment costs.

Initial evaluation of FT catalysts for slurry bubble column reactors is performed in bench-scale, mechanically-stirred, slurry reactors. These reactors offer excellent temperature control and flexibility in operating conditions. Descriptions of such reactors and their operation are available [8]. Since the internal composition of such reactors is uniform, they facilitate development of kinetic models without the complications involved in the analysis of integral data obtained in a fixed bed reactor. The kinetic models will permit the prediction of performance of the catalyst in a slurry-bubble column reactor.

The production of hydrocarbons using traditional FT catalysts, such as Fe or Co, is governed by chain growth or polymerization kinetics. This can be described by the Anderson formalism [9], which is related to the Schulz-Flory polymerization equation [10]. The nature of the product and the product distribution among the carbon numbers will depend upon the catalytic surface, composition (H_2/CO ratio) and the rate of flow of the feed gas, reaction pressure, and the temperature at which the FT synthesis reaction is performed. The above parameters will affect the rate of hydrogen and CO dissociation, hydrogenation, degree of polymerization, and desorption of the product species.

Chain Growth Kinetics: The chain growth probability is designated by the quantity α and represents the probability that an oligomer with $(r-1)$ carbon atoms will grow to an oligomer with r carbon atoms. The product distribution among the carbon numbers follows the polymerization equation

$$W_n = n(1-\alpha)^2 \alpha^{n-1} \quad (4)$$

The above expression, usually known as the Anderson-Schultz-Flory (ASF) polymerization equation, is written

$$\log(W_n/n) = n \log \alpha + \log[(1-\alpha)^2/\alpha] \quad (5)$$

One would then expect a linear relation between $\log(W_n/n)$ and n , with slope $\log \alpha$, as shown in Fig. 1 [4]. The theoretical maxima for various hydrocarbon fractions in the FT product such as gas, naphtha, heavy distillate, and wax have been calculated [11] and can be seen in Fig. 2.

Catalyst Synthesis

Varieties of iron catalysts have been examined for FT synthesis in slurry reactors. These include (1) precipitated iron catalysts [3-5,12,13], (2) fused iron catalysts [14-16], (3) ultrafine-particle catalysts [17-19], and (4) catalysts produced by laser pyrolysis [20,21].

The pioneering work of Kolbel in Germany to develop the Rheinpreussen slurry reactor process after World War II used a precipitated iron catalyst [3]. The results obtained by Kolbel were very favorable, and efforts are ongoing to reproduce the space-time yields or catalyst activities. Koppers [22] of Rheinprussen claimed slurry reactor space-time yields of up to 2800 kg/m³ per day in a laboratory reactor, but all other studies published by his group reported considerably lower values (e.g., 940 kg/m³ per day in a pilot-scale reactor and 740 kg/m³ per day in a laboratory reactor [23]). These investigations and later work by the Mobil group [4,5] using precipitated iron catalysts in a slurry bubble column reactor (see Table 1) have resulted in a sustained interest in this type of catalyst. Accordingly, the effort in the DOE program has been centered on precipitated iron catalysts.

Precipitated Iron Catalysts:

The development of precipitated iron catalysts for slurry-phase synthesis was based on earlier work that was performed with iron catalysts intended for use in fixed-bed processes [1]. The feasibility of the use of precipitated iron catalysts has been demonstrated under relatively mild Arge-type conditions at SASOL [1,24]. Apart from the tests conducted on a limited scale at Rheinpreussen [3] and Mobil [4,5], these catalysts have not been sufficiently demonstrated in a slurry-bubble column reactor representative of commercial operation. The main reason for this is the lack of precise information in the public domain regarding the following factors influencing the activity, selectivity, and stability of the catalysts: (1) pH of precipitation, (2) concentration of Fe and other components such as Cu in the precipitation reactor, (3) temperature of precipitation, (4) residence time of Fe and other components in the precipitation reactor, (5) filtration rate of the hydrated gel, (6) washing rate of the hydrated iron oxide gel, (7) use of binders such as silica to provide mechanical strength, and (8) procedures such as spray drying to obtain uniform size spherical particles with a mean diameter of about 30 microns.

Under the DOE program an iron-based catalyst with the desired properties has been developed [25] for study in the Alternative Fuels Development Unit in LaPorte, Texas. Efforts are underway to scaleup the synthetic procedure in order to make about 2,000 pounds of the catalyst. Some features of the catalyst are (1) spherical particles of average diameter of about 30 microns, (2) FT and WGS activities that are higher than those of the commercial Ruhrchemie Fe catalyst, and (3) favorable suspension behavior in the slurry medium.

Kinetics of the Fischer-Tropsch Synthesis over Fe Catalysts

The CSTR is well-suited for measuring the intrinsic kinetics of the FT reaction as the influence of heat and mass transfer effects in this reactor can be ignored [8]. The kinetic models that have been proposed for the FT reaction will now be examined.

To date, no model can account for the reaction rate under all conditions. Each of the models agrees with the experimental results under certain conditions.

Anderson's rate expression [9]

$$-r_{CO-H_2} = \frac{k P_{H_2}}{1 + a P_{H_2O}/P_{CO}} \quad (6)$$

is applicable when the WGS activity is low. The rate expression is suggestive of a competition between water and CO for the available sites on the catalyst.

Ledakowicz et al. [26] have proposed that the rate expression

$$-r_{CO-H_2} = \frac{k P_{H_2}}{1 + a P_{CO_2}/P_{CO}} \quad (7)$$

could be used at high WGS activity. This rate equation implies that the influence of CO_2 is more important than that of H_2O under these conditions.

Satterfield et al. [27] drew attention to the fact that water inhibits the FT synthesis rate more than does CO_2 . It was therefore reasonable to suppose that the concentration of H_2O (or the H_2O/H_2 ratio) is more important than the concentration of CO_2 (or the CO_2/CO ratio) in affecting the oxidation state of the catalyst. It was suggested [28] that the inhibition attributed to CO_2 by Ledakowicz et al. [26] was instead actually caused by H_2O formed by the reverse WGS reaction. Based on these arguments, the following rate equation [29] was favored:

$$-r_{CO-H_2} = \frac{k P_{H_2}}{1 + a P_{H_2O}/(P_{H_2} \cdot P_{CO})} \quad (8)$$

To use equation (8), it is important to have reliable methods for analyzing H_2O and H_2 . H_2O tends to tail in some GC columns, but methods to quantitatively determine the H_2O concentration have been established [30]. The kinetics of the FT synthesis has recently been reviewed by Wojciechowski [31].

In addition to fluid dynamic data, the development of reliable kinetic rate expressions for iron catalysts is important for the prediction of the behavior of slurry bubble column reactors. The ongoing research to develop active and stable Fe FT catalysts for the slurry phase will stimulate additional work to develop accurate kinetic rate expressions.

Predicting Catalytic Performance in a Slurry Bubble Column Reactor

From CSTR data obtained on a precipitated iron catalyst, Abrevaya and Shah [12] have predicted the performance in an SBCR. The calculation was based on the $CO+H_2$ conversion measured in a CSTR at 265°C and 275°C at various feed flowrates (Fig 3). They assumed that the slurry bubble column reactor could be modelled as 11 slurry autoclave reactors-in-series operating at 8%, 16%, 24% ... 88% conversions. Since data were not available below 35% conversion at 265°C and 50% at 275°C (Fig 3), it was assumed that the reaction rate and selectivity at these temperatures did not

Table 1

Comparative Catalyst Performance Data

Reactor Type*	SASOL (Dry, 1981)		Köbel et al. (1955) Rheinpreussen Plant	Sakai and Kunugi (1974) [32]	MOBIL (Kuo, 1985)	
	Arge	Synthol			CT 256-3 Low Wax	CT 256-13 High Wax
Catalyst	Pptd. FB	Fused CFB	100Fe/0.1Cu/.05- 0.5% O BCSR	100Fe/0.3Cu/.6- 1.2% O BCSR	Fe/Cu/K ₂ O BCSR	Fe/Cu/K ₂ O BCSR
Conditions						
Temperature, °C	220	325	268	273	260	258
Pressure, atm	25	25	12	10.8	15	15
SV, ML/g-Fe/h	--	--	3.4	12.1	2.6	2.4
H ₂ :CO ratio	1.3-2.0	>2.0	0.67	0.52	0.67	0.67
Activity						
CO+H ₂ conv. (%)	--	--	89.0	78.5 (CO)	86.8	82.2
mol/g-cat/h	--	--	.106	--	.070	.061
Nm ³ /kg-Fe/h	--	--	3.02	--	2.25	1.97
Selectivity, wt%						
C ₁	2.0	10.6	3.2 (CH ₄ +C ₂ H ₆)	2.3	7.8	2.7
C ₂ -C ₄	11.2	35.2	31.3	8.2	24.5	11.1
C ₅ -C ₁₁	18.6	42.5	53.6	4.7 (C ₅ -C ₉)	41.9	18.1
C ₁₂ -C ₁₈	14.5	7.5	10.0	12.8 (C ₁₀ -C ₁₈)	15.4	10.2
C ₁₉ +	53.7	4.2	1.9	71.9	10.8	57.9
C ₁₂ +	68.2	11.7	11.9	84.7 (C ₁₀ .)	26.2	68.1
Product Yield						
g-HC/Nm ³ converted	--	--	178	151.8	197	206
g-HC/g-Fe/h	--	--	.57	--	.37	.41

* FB - fixed bed, CFB - circulating fluidized bed, BCSR - bubble column slurry reactor

change below 35% and 50% conversion respectively. The calculations made using these assumptions are summarized in Table 2. Subsequent improvements in the catalyst resulted in catalyst performance that was much closer to the target performance.

Table 2

Performance of Precipitated Iron Catalyst [12] in
11 Autoclave Reactors in Series at 21 ATM, 0.7 H₂: CO Feed
(wt-%)

	<u>265° C</u>	<u>275° C</u>	<u>Target</u>
C ₁	4.3	5.8	---
C ₂ (Ethane + Ethylene)	4.6	6.0	---
C ₁ + C ₂	8.9	11.8	7
Sv, nL/h-gFe	1.1	1.6	≥2

Concluding Remarks:

From the survey on Fe FT catalysts for slurry-phase operation, it is evident that additional research is needed for the development of reproducible synthesis of active and stable catalysts. A more complete understanding of the behavior of iron catalysts that can be obtained from modern surface and bulk analytic techniques is required. The correlation of catalyst properties with kinetic data will establish a sound basis for the commercial manufacture of Fe FT catalysts for slurry bubble column reactors.

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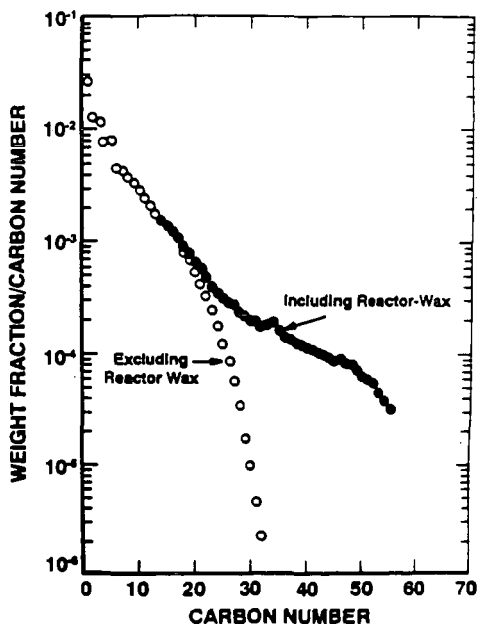


Figure 1. Schulz-Flory distribution for Fischer-Tropsch products from a slurry bubble column-reactor [4].

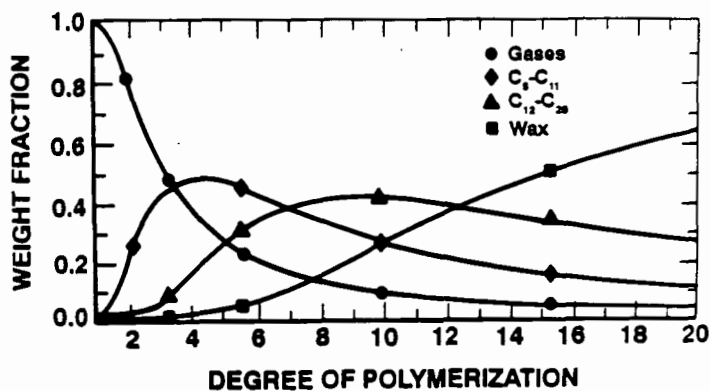


Figure 2. FT product distribution versus degree of polymerization [11].

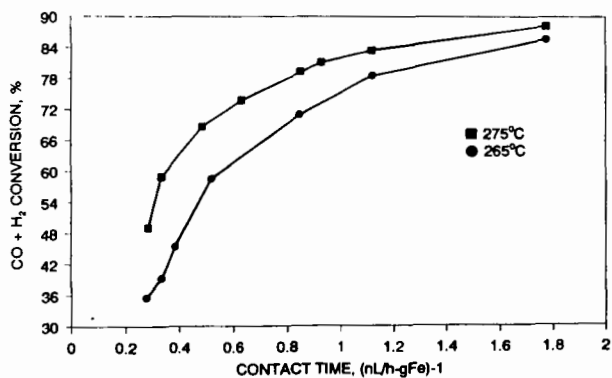


Figure 3. Conversion versus contact time for a precipitated iron catalyst [12] at 21 atm with feed $H_2/CO = 0.7$.